Quality Assurance

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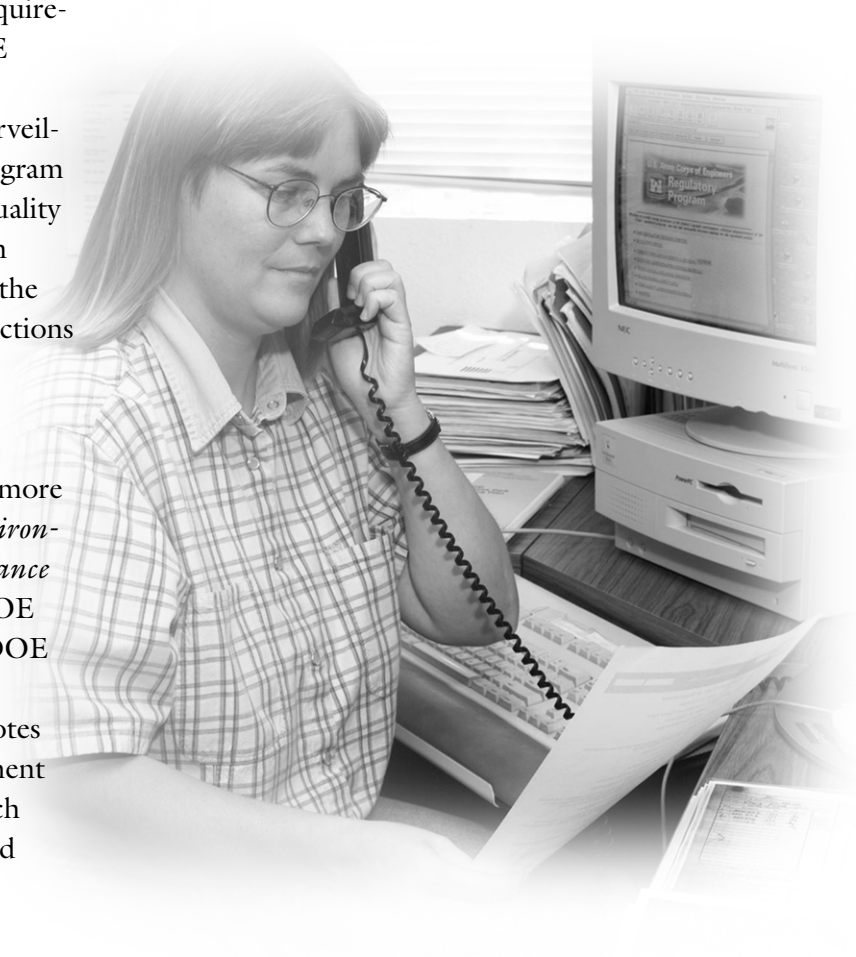
Introduction

Quality assurance (QA) is a system of activities and processes put in place to ensure that monitoring and measurement data meet user requirements and needs. Quality control (QC) consists of procedures used to verify that prescribed standards of performance in the monitoring and measurement process are met. U.S. Department of Energy (DOE) orders and guidance mandate QA requirements for environmental monitoring of DOE facilities. DOE Order 5400.1 identifies QA requirements for radiological effluent and surveillance monitoring and specifies that a QA program consistent with the DOE order addressing quality assurance is established. This order sets forth policy, requirements, and responsibilities for the establishment and maintenance of plans and actions that assure quality in DOE programs.

Lawrence Livermore National Laboratory conducted QA activities in 2000 at the Livermore site and Site 300 in accordance with the *Environmental Protection Department Quality Assurance Management Plan* (Revision 3), based on DOE Order 5700.6C, which meets the intent of DOE Order 0-414.1A and prescribes a risk-based, graded approach to QA. This process promotes the selective application of QA and management controls based on the risk associated with each activity in order to maximize effectiveness and efficiency in resource use.

The DOE *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (U.S. DOE 1991) requires that an environmental monitoring plan be prepared. LLNL environmental monitoring is conducted according to procedures published in Appendix B of the LLNL *Environmental Monitoring Plan* (Tate et al. 1999).



LLNL or commercial laboratories analyze environmental monitoring samples using U.S. Environmental Protection Agency (EPA) standard methods, when available. When EPA standard methods are not available, custom analytical procedures (usually developed at LLNL) are used. The radiochemical methods used by LLNL laboratories are described in procedures unique to the laboratory performing the analyses. LLNL uses only State of California-certified laboratories to analyze its environmental monitoring samples. In addition, LLNL requires all analytical laboratories to maintain adequate QA programs and documentation of methods.

Quality Assurance Activities

Nonconformance reporting and tracking is an LLNL QA process for ensuring that Environmental Protection Department (EPD) activities meet the department's QA requirements and that problems are found, identified, resolved, and prevented from recurring. LLNL generated 76 Nonconformance Reports (NCRs) related to environmental monitoring in 2000 compared to 111 in 1999 and 92 in 1998. The number of NCRs decreased in 2000 because of a change in EPD reporting requirements. Beginning in the summer of 2000, EPD no longer required the documentation of samples that were planned but not successfully collected and analyzed. The reason for lost samples is documented on paperwork completed during sampling, and a summary of these results appears in **Table 14-1**.

Thirty-nine of the 76 NCRs generated in 2000 were due to problems with analytical laboratories. Twenty-one were due to documentation or procedural errors. Three were related to minor problems with air-monitoring equipment, and another five were due to minor problems with sewer monitoring equipment. The remaining NCRs were related to location changes (4) and shipping problems (1).

LLNL addresses analytical laboratory problems with the appropriate laboratory as they arise. Many of the NCRs written in response to problems with the laboratories concerned minor documentation or paperwork errors, which were corrected soon after they were identified. Other problems—such as missed holding times, late analytical results, and typographical errors on data reports—accounted for the remaining NCRs related to the analytical laboratories. The majority of these problems were corrected by reanalysis, resampling, reissued reports, or corrected paperwork and associated sample results were not affected.

LLNL addresses internal documentation, training, and procedural errors by conducting formal and informal training. These errors generally do not result in lost samples, but may require extra work on the part of sampling and data management personnel to resolve or compensate for the errors.

Analytical Laboratories

LLNL continued to operate under the Blanket Service Agreements (BSAs) put into place with seven analytical laboratories in March 1999. LLNL continues to work closely with these analytical laboratories to minimize the occurrence of problems.

Participation in Laboratory Intercomparison Studies

The LLNL Chemistry and Materials Science Environmental Services' (CES) Environmental Monitoring Radiation Laboratory (EMRL) and the Hazards Control Department's Analytical Laboratory (HCAL) participated in the DOE Environmental Monitoring Laboratory (EML) intercomparison studies program. A review of the EML studies indicates that 45 of 46 results reported by CES and 10 of 10 results reported by HCAL fell within the established acceptance control limits.

Table 14-1. Sampling completeness in 2000 for the Livermore site and Site 300

Environmental monitoring network	Number of analyses planned	Number of analyses completed	Complete-ness (%)	Reason(s) for lost samples
Air particulate (Livermore site)				
Radiological parameters	1208	1182	98	Lost power due to auto accident (23), unacceptable flow rate (2), motor failure (1)
Beryllium	96	96	100	
Air particulate (Site 300)				
Radiological parameters	715	691	97	Lost power due to electrical upgrade (18), unit off on arrival (4), no access to area (2)
Beryllium	72	69	96	Lost power due to electrical upgrade (3)
Air tritium				
Livermore site and vicinity	476	445	93	Lost power due to auto accident (9), flask broke (12), insufficient run time (6), excessive flow (4)
Site 300	26	25	96	Insufficient run time (1)
Soil				
Livermore	42	42	100	
Site 300	30	30	100	
Arroyo sediment (Livermore site only)	63	51	81	Could not access sampling location (12)
Vegetation				
Livermore site and vicinity	70	70	100	
Site 300	32	32	100	
Wine	25	25	100	
Rain				
Livermore site	118	97	82	Insufficient rainfall (20) bucket stolen (1)
Site 300	24	10	42	Insufficient rainfall (14)
Storm water runoff				
Livermore site	458	218	48	Two storms not sampled due to lack of runoff (226), sampler error (8), analytical lab error (6)
Site 300	148	82	55	No flow at locations (66)

Table 14-1. Sampling completeness in 2000 for the Livermore site and Site 300 (continued)

Environmental monitoring network	Number of analyses planned	Number of analyses completed	Completeness (%)	Reason(s) for lost samples
Drainage Retention Basin				
Field measurements	886	835	94	Lake drained (48), sampler error (3)
Samples	90	86	96	Sampler error (4)
Releases	63	63	100	
Other surface water (Livermore only)	60	60	100	
Groundwater				
Livermore site	488	470	96	Missed samples (18)
Site 300	2069	1933	93	Well dry (72), equipment problems (42), well inaccessible because of construction (14), sampler error (9)
Livermore Valley wells	29	24	83	Sample not provided (4), well not operational (1)
Sewage				
B196	912	910	99.8	Loss of flow (2)
C196	329	329	100	
LWRP[a] effluent	128	128	100	
Digester sludge	80	80	100	
WDR-96-248				
Surface impoundment wastewater	60	58	97	Missed sampling event (2)
Surface impoundment groundwater	105	105	100	
Sewage ponds wastewater	45	45	100	
Sewage ponds groundwater	144	144	100	
Thermoluminescent dosimeters (TLDs)				
Livermore site	76	76	100	
Livermore Valley	100	95	95	Samples missing at time of pickup
Site 300	74	65	88	Samples lost due to vehicle fire
Cooling towers (Site 300 only)	40	38	95	Tower off-line (2)

a LWRP = Livermore Water Reclamation Plant

CES EMRL participated in two DOE Mixed Analyte Performance Evaluation Program (MAPEP) studies in 2000. Twenty-one of twenty-two analytes reported fell within acceptable limits.

CES has implemented changes that are intended to address the root causes of unacceptable intercomparison study results and prevent future results from falling outside the acceptance control limits.

Details of the intercomparison study results, including the follow-up explanation and response for data that fell outside the acceptance control limits, are presented in the Data Supplement. Although contract laboratories are also required to participate in laboratory intercomparison programs, permission to publish their results for comparison purposes was not granted for 2000.

LLNL uses the results of intercomparison program data to identify and monitor trends in performance and to solicit corrective action responses for unacceptable results. If a laboratory performs unacceptably for a particular test in two consecutive performance evaluation studies, LLNL may choose to select another laboratory to perform the affected analyses until the original laboratory can demonstrate that the problem has been corrected. Continued unacceptable performance could result in formal notification or suspension, depending on the type of laboratory. If an off-site laboratory continues to perform unacceptably or fails to prepare and implement acceptable corrective action responses, the LLNL Procurement Department will formally notify the laboratory of its unsatisfactory performance. If the problem persists, the off-site laboratory's BSA could be terminated. If an on-site laboratory continues to perform unacceptably, use of that laboratory could be suspended until the problem is corrected.

A joint performance evaluation committee composed of members from EPD, CES, and Lawrence Berkeley National Laboratory is creating a systematic process for evaluating laboratory performance using performance evaluation samples. A method for evaluating the results of intercomparison studies will be developed by that committee.

Duplicate Analyses

Duplicate or collocated samples are distinct samples of the same matrix collected as closely to the same point in space and time as possible. Collocated samples processed and analyzed *by the same laboratory* provide intralaboratory information about the precision of the entire measurement system, including sample acquisition, homogeneity, handling, shipping, storage, preparation, and analysis. Collocated samples processed and analyzed *by different laboratories* provide interlaboratory information about the precision of the entire measurement system (U.S. EPA 1987). Collocated samples may also be used to identify errors such as mislabeled samples or data entry errors.

Tables 14-2 through **14-4** present statistical data for collocated sample pairs, grouped by sample matrix and analyte. Samples from both the Livermore site and Site 300 are included. **Tables 14-2** and **14-3** are based on data pairs in which both values are detections (see Statistical Methods in this chapter). **Table 14-4** is based on data pairs in which either or both values are nondetections.

Precision is measured by the percent relative standard deviation (%RSD); see the EPA's *Data Quality Objectives for Remedial Response Activities: Development Process*, Section 4.6 (U.S. EPA 1987). Acceptable values for %RSD vary greatly with matrix, analyte, and analytical method;

Table 14-2. Quality assurance collocated sampling. Summary statistics for analytes with more than eight pairs in which both results were above the detection limit.

Matrix	Analyte	N[a]	%RSD[b]	Slope	r^{2}[c]	Intercept
Air	Gross beta	14	9.17	1.09	0.87	–0.000112 Bq/m^3
	Beryllium	16	13.7	1.02	0.99	–1.44 pg/m^3
	Uranium-234+233[d]	12	37.7	0.15	0.1	3.17×10^{-7} Bq/m^3
	Uranium-235+236[e]	11	78.3	1.1	0.52	-2.03×10^{-8} Bq/m^3
	Uranium-238[d]	12	45.6	0.194	0.13	2.62×10^{-7} Bq/m^3
	Tritium	20	20.7	0.904	1.0	0.00278 Bq/m^3
Groundwater	Gross beta	19	12.5	1.01	0.98	0.00858 Bq/L
	Arsenic	20	13.3	1.03	0.99	–0.000658 mg/L
	Barium	10	8.29	1.02	0.98	0.00383 mg/L
	Nitrate (as NO_3)	24	2.86	0.96	0.98	2.82 mg/L
	Potassium	30	3.51	0.958	0.98	0.168 mg/L
	Trichloroethene	11	3.1	1.0	1.0	0.276 μg/L
	Tritium	15	5.81	1.01	1.0	25.1 Bq/L
	Uranium-234+233	20	7.7	1.02	0.99	0.00506 Bq/L
	Uranium-238	18	8.15	0.994	0.99	0.00716 Bq/L
	Vanadium	9	1.43	0.787	0.84	0.0123 mg/L
Sewer	Gross alpha[e]	9	24.8	0.192	0.05	0.000121 Bq/mL
	Gross beta	52	10.2	0.976	0.97	8.33×10^{-6} Bq/mL

a Number of collocated pairs included in regression analysis

b 75^{th} percentile of percent relative standard deviations (%RSD) where %RSD $= \left(\frac{200}{\sqrt{2}}\right)\frac{|x_1 - x_2|}{x_1 + x_2}$ and x_1 and x_2 are the reported concentrations of each routine-duplicate pair

c Coefficient of determination

d Outside acceptable range of slope or r^2 because of outliers

e Outside acceptable range of slope of r^2 because of variability

however, lower values represent better precision. The results for %RSD given in **Table 14-2** are the 75^{th} percentile of the individual precision values.

Regression analysis consists of fitting a straight line to the collocated sample pairs. Good agreement is indicated when the data lie close to a line with slope equal to 1 and intercept equal to 0, as illustrated in **Figure 14-1**. Allowing for normal analytical variation, the slope of the fitted line should be between 0.7 and 1.3, and the absolute value of the intercept should be less than the detection limit. The coefficient of determination (r^2) should be greater than 0.8. These criteria apply to pairs in which both results are above the detection limit.

When there were more than eight data pairs with both results in each pair considered detections, precision and regression analyses were performed;

Table 14-3. Quality assurance collocated sampling. Summary statistics for selected analytes with eight or fewer pairs in which both results were above the detection limit.

Matrix	Analyte	N	Mean ratio	Minimum ratio	Maximum ratio
Aqueous	Gross beta	1	1.1	1.1	1.1
Groundwater	Gross alpha	7	1.3	0.88	2.1
	Americium-241	1	1.3	1.3	1.3
	Plutonium-238	1	1.1	1.1	1.1
	Plutonium-239+240	2	1.5	1.5	1.5
	Radium-226	5	1.1	0.62	2.0
	Uranium-235+236	7	1.0	0.84	1.3
Runoff (from rain)	Gross alpha	3	0.63	0.39	0.96
	Gross beta	5	1.0	0.94	1.2
	Uranium-234+233	1	0.89	0.89	0.89
	Uranium-238	1	0.93	0.93	0.93
Soil	Beryllium-7	1	0.94	0.94	0.94
	Cesium-137	4	1.6	0.85	3.7
	Potassium-40	4	0.96	0.88	1.0
	Plutonium-239+240	3	1.2	0.92	1.5
	Radium-226	4	0.97	0.95	1.0
	Radium-228	4	0.97	0.91	1.0
	Thorium-232	4	0.98	0.92	1.1
	Uranium-235	4	1.0	0.92	1.2
	Uranium-238	4	0.93	0.66	1.3
Sewer	Tritium	8	1.0	0.83	1.6
	Plutonium-239+240	2	1.2	1.2	1.2
Vegetation	Tritium	2	0.86	0.85	0.87

those results are presented in **Table 14-2**. When there were eight or fewer data pairs with both results above the detection limit, the ratios of the individual duplicate sample pairs were averaged; the average, minimum, and maximum ratios for selected analytes are given in **Table 14-3**. The mean ratio should be between 0.7 and 1.3.

When one of the results in a pair is a nondetection, then the other result should be less than two times the detection limit. **Table 14-4** identifies the sample media and analytes for which at least one pair failed this criterion. Analytes with fewer than four pairs are omitted from the table.

Table 14-4. Quality assurance duplicate sampling. Summary statistics for analytes with at least four pairs in which one or both results were below the detection limit.

Media	Analyte	Number of inconsistent pairs	Number of pairs	Percent of inconsistent pairs
Air	Tritium	1	28	3.6
Groundwater	Gross alpha	2	19	11
	Gross beta	1	7	14
	Americium-241	2	8	25
	2-Amino-4,6-dinitrotoluene	2	5	40
	Lead	1	26	3.8
	Methylene chloride	1	26	3.8
	Nitrite (as N)	1	6	17
	Nitrite (as NO_2)	1	4	25
	Plutonium-238	4	20	20
	Plutonium-239+240	8	44	18
	Plutonium-239+240	8	44	18
	Zinc	1	25	4
Rain	Tritium	1	5	20
Sewer	Gross alpha	16	43	2.3
	1,1,1-Trichloroethane	1	7	14

Collocated sample comparisons are more variable when the members of the pair are analyzed by different methods or with different criteria for analytical precision. For example, radiological analyses using different counting times or different laboratory aliquot sizes will have different amounts of variability.

These analyses show generally good agreement between routine samples and QA duplicates: 90% of the pairs have a precision better than 26%. Data sets not meeting our precision criteria fall into one of two categories. The first category, outliers, can occur because of data transcription errors, measurement errors, or real but anomalous results. Of the 18 data sets reported in **Table 14-2**, 2 did not meet the criterion for acceptability because of outliers. **Figure 14-2** illustrates a set of collocated pairs with one outlier.

The other results that do not meet the criterion for acceptability consist of data sets where there is a lot of scatter. This tends to be typical of nondetections and measurements at extremely low concentrations, as illustrated in **Figure 14-3**. Low concentrations of radionuclides on particulates in air highlight this effect, because one or two radionuclide-containing particles on an air filter can

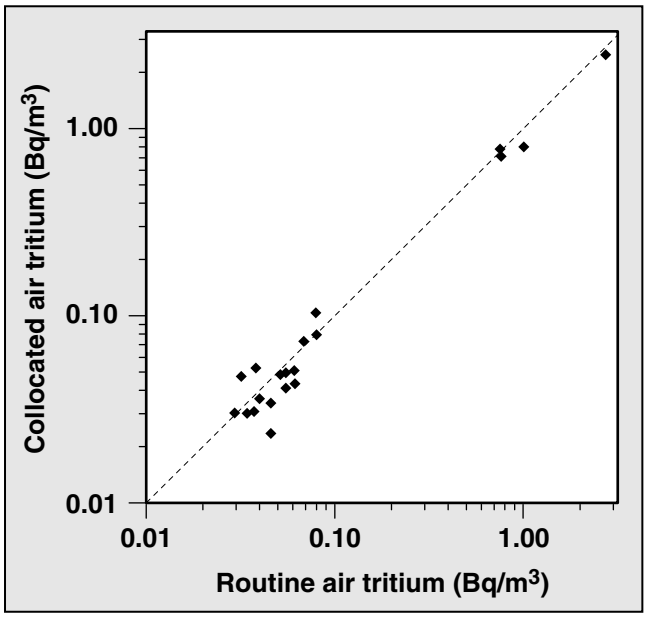


Figure 14-1. Air tritium concentrations from collocated samples. These samples lie close to a line with slope equal to 1 and intercept equal to 0.

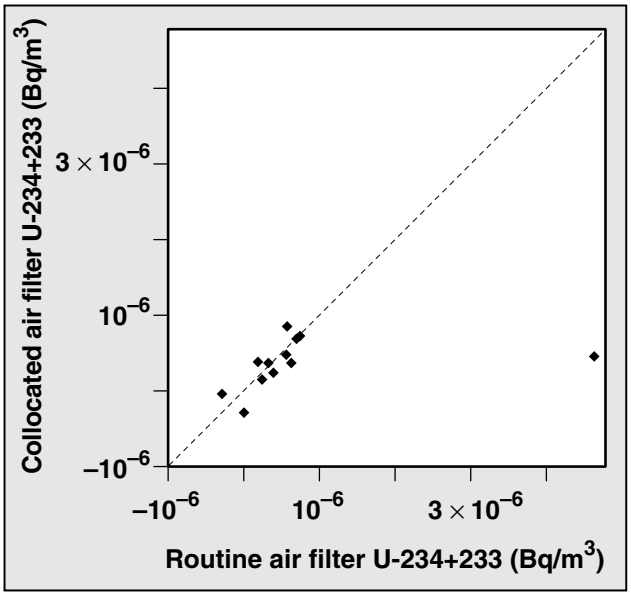


Figure 14-2. Air uranium concentrations from collocated samples showing an outlier

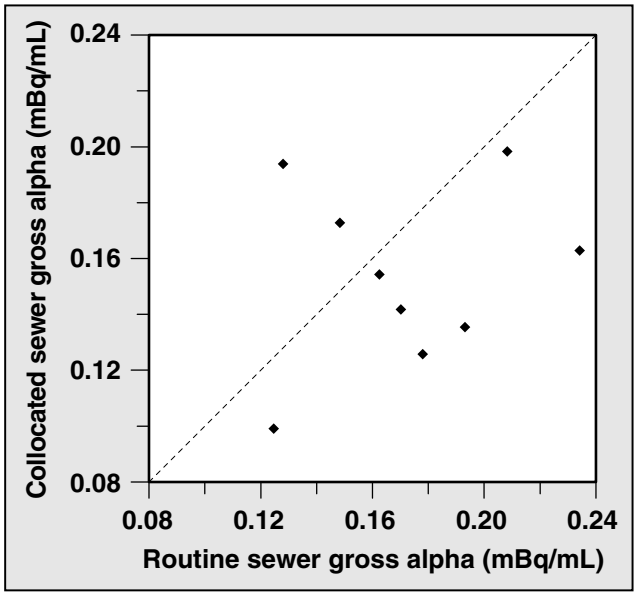


Figure 14-3. Sewer gross alpha concentrations from collocated samples showing a lot of scatter

significantly affect results. Other causes of high variability are sampling and analytical methodology. Analyses of total organic carbon and total organic halides in water are particularly difficult to control. Of the 18 data sets in **Table 14-2**, two show sufficient variability in results to make them fall outside the acceptable range.

Statistical Methods

Statistical methods used in this report have been implemented in accordance with the *Environmental Monitoring Plan* (Tate et al. 1999). These methods reduce the large volumes of monitoring data to summary estimates suitable for temporal and spatial comparisons. Attention is given to estimating accuracy, bias, and precision of all data.

Data review and analysis are conducted in accordance with the *Environmental Monitoring Plan* (Tate et al. 1999) and the data analysis procedure developed by EPD's Operations and Regulatory

Affairs Division. These documents contain detailed information regarding the acceptability of data and the procedures that are followed for the identification, notification, and correction of suspect data.

Radiation Units

Data for 2000 have been reported in Système Internationale (SI) units to conform with standard scientific practices and federal law. Values in the text are reported in becquerels (Bq) and millisieverts (mSv); equivalent values in picocuries (pCi) and millirems (mrem) are given in parentheses.

Radiological Data

The precision of radiological analytical results is displayed in the Data Supplement tables as the 2σ counting uncertainty. The counting uncertainties are not used in summary statistic calculations. Any radiological result exhibiting a 2σ counting uncertainty greater than or equal to 100% is considered to be a nondetection. The reported concentration is derived from the number of sample counts minus the number of background counts. Therefore, a sample with a low concentration may have a negative value; such results are reported in the tables and used in the calculation of summary statistics and statistical comparisons.

Some Data Supplement tables provide radioactivity sensitivity values instead of a reported concentration when the radiological result is below the detection criterion. Such results are displayed in the tables with a less-than symbol. These values can be described as a concentration of radioactive material that can be detected (distinguished from background) with a large degree of confidence. These radioactivity sensitivity values are referred to as minimum detectable concentrations (MDC) in Chapters 4 and 5, limits of sensitivity (LOS) in Chapter 6, and detection limits (DL) in Chapters 7 and 9.

Nonradiological Data

Nonradiological data reported as being below the reporting limit are also displayed in the tables with a less-than symbol. The reporting limit values are used in the calculation of summary statistics, as explained below.

Statistical Comparisons

Standard comparison techniques (such as regression, t-tests, and analysis of variance) have been used where appropriate to determine the statistical significance of trends or differences between means. When such a comparison is made, it is explicitly stated in the text as being "statistically significant" or "not statistically significant." Other uses of the word "significant" in the text do not imply that statistical tests have been performed. Instead, these uses relate to the concept of practical significance and are based on professional judgment.

Summary Statistics

Determinations of measures of central tendency and associated measures of dispersion are calculated according to the *Environmental Monitoring Plan* (Tate et al. 1999). For data sets that do not contain values below the detection criterion, the measures of central tendency and dispersion are the median and interquartile range (IQR). The IQR is the range that encompasses the middle 50% of the data set. The IQR is calculated by subtracting the 25th percentile of the data set from the 75th percentile of the data set. When necessary, the percentiles are interpolated from the data. Software vendors may use slightly different formulas for calculating percentiles. Radiological data sets that include values less than zero may have an IQR greater than the median.

For data sets with one or more, but fewer than one-half, of the values below the detection criterion, the measure of central tendency is the median. If the values of the detection limits and the number of values below the detection limit permit (determined on a case-by-case basis), dispersion is reported as the IQR. Otherwise, no measure of dispersion is reported. Statistics are calculated using the reported detection limit value for nonradiological data or the reported value for radiological data.

For data sets with one-half or more of the values below the detection criterion, the central tendency is reported as less than the median value. Dispersion is not reported.

Quality Assurance Process for the Environmental Report

Unlike the preceding discussion, which focused on standards of accuracy and precision in data acquisition and reporting, a discussion of QA/QC procedures for a technical publication per se must deal with how to retain content accuracy through the publication process. Because publication of a large, data-rich document like this site annual environmental report involves many operations and many people, the chances of introducing errors are great. At the same time, ensuring quality is more difficult because a publication is less amenable to the statistical processes used in standard quality assurance methods.

The QA procedure we used concentrated on the tables and figures in the report and enlisted 40 authors, contributors, and technicians to check the accuracy of sections other than those they had authored or contributed to. In 2000, the 92 illustrations and 66 tables in the main volume and the 117 tables in the Data Supplement were checked. Checkers were assigned illustrations and tables and given a copy of each item they were to check along with a quality control form to fill out as they checked the item. Items to be checked included figure captions and table titles for clarity and accuracy, data accuracy and completeness, figure labels and table headings, units, significant digits, and consistency with text. When checking numerical data, checkers randomly selected 10% of the data and compared it to values in the master database. If all 10% agreed with the database, further checking was considered unnecessary. If there was disagreement in the data, the checker compared another 10% of the data with the database values. If more errors were found, the checker had then to verify every piece of data in the table or illustration.

A coordinator guided the process to ensure that forms were tracked and the proper approvals were obtained. Completed quality control forms and the corrected illustrations or tables were returned to the report editors, who were responsible for ensuring that changes, with the agreement of the original contributor, were made. This QA check resulted in the correction of data errors and omissions on 10% of the illustrations, 33% of the tables in the main volume, and 39% of the tables in the Data Supplement. Other corrections were made to footnotes, headings, titles in tables, graph axes, callouts, and captions in figures.